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Wednesday, September 22, 1999

Assistant Commissioner for Patents
Box PATENT APPLICATION
Washington, D.C. 20231



TO THE ASSISTANT COMMISSIONER FOR PATENTS

1. Type of Application

Transmitted herewith for filing is an original patent application of the inventors:

PAUL M. McELFRESH, and CHAD F. WILLIAMS for:

HYDRAULIC FRACTURING USING NON-IONIC SURFACTANT GELLING AGENT

(Attorneys' Docket No. 304-15027-US).

2. Benefit of Prior U.S. Application(s)

☐ Please amend the specification by inserting on page 1, after the title in line 1 but before the "Field of the Invention" in line 3, the following sentence:

--This application claims the benefit of U.S. Provisional Application No. 60/____
____ filed ____--

3. Papers Enclosed

Enclosed are:

- ☒ two sheets of formal drawings;
- ☒ a patent application (12 pages, including 4 pages of claims; and 1 abstract page);
- ☒ an assignment of the invention to Baker Hughes Incorporated;
- ☒ Assignment Recordal Form Cover Sheet (\$40.00 recordal fee authorized charged to deposit account therein);
- ☐ a certified copy of a _____ application;
- ☒ a Declaration and power of attorney executed by the inventor(s);
- ☐ Statement of Disclosure under 37 CFR §1.56;
- ☒ a Certificate of Mailing by "Express Mail" under 37 CFR §1.10;

Express Mailed with Label No. EE709364231US on 9/22/99.

☐ a declaration, power of attorney and assignment will be filed in due course in accordance with 37 CFR §1.53(d).

4. Fee Calculation

Claims as Filed				
For:	#Filed	#Extra	Rate	Fee
Total Claims	17-20=	0	x \$18.00=	0.00
Independent Claims	3-3=	0	x \$78.00=	0.00
Basic Fee:				<u>\$760.00</u>
Total Filing Fee:				\$760.00

5. Method of Payment of Fee

The payment of the filing fee of \$760.00 and assignment recordal of \$___ for a total of \$760.00 is accomplished herein by one of the following methods:

☒ Please charge the filing fee to Deposit Account No. 02-0429.

☒ A duplicate copy of this sheet is enclosed.

☒ Authorization to charge assignment recordal fee is given in the separate Assignment Recordal Form Cover Sheet (enclosed).

☒ The Commissioner is hereby authorized to charge payment of the following fees during the pendency of this application or credit any overpayment to Deposit Account No. 02-0429. A duplicate copy of this sheet is enclosed.

☒ Any filing fees under 37 CFR §1.16 for presentation of extra claims.

☒ Any patent application processing fees under 37 CFR §1.17.

☐ The issue fee set in 37 CFR §1.18 at or before mailing of the Notice of Allowance, pursuant to 37 CFR §1.311(b).

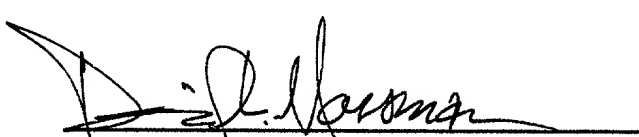
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SEPTEMBER 22, 1999

Date


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HYDRAULIC FRACTURING USING NON-IONIC SURFACTANT GELLING AGENT

Field of the Invention

The present invention relates to treatment fluids used during petroleum recovery operations, and more particularly relates, in one embodiment, to methods of using treatment fluids containing gelling agents during petroleum recovery operations.

Background of the Invention

Hydraulic fracturing is a method of using pump rate and hydraulic pressure to fracture or crack a subterranean formation. Once the crack or cracks are made, high permeability proppant, relative to the formation permeability, is pumped into the fracture to prop open the crack. When the applied pump rates and pressures are reduced or removed from the formation, the crack or fracture cannot close or heal completely because the high permeability proppant keeps the crack open. The propped crack or fracture provides a high permeability path connecting the producing wellbore to a larger formation area to enhance the production of hydrocarbons.

The development of suitable fracturing fluids is a complex art because the fluids must simultaneously meet a number of conditions. For example, they must be stable at high temperatures and/or high pump rates and shear rates which can cause the fluids to degrade and prematurely settle out the proppant before the fracturing operation is complete. Various fluids have been developed, but most commercially used fracturing fluids are aqueous based liquids which have either been gelled or foamed. When the fluids are gelled, typically a polymeric gelling agent, such as a solvatable polysaccharide is used. The thickened or gelled fluid helps keep the proppants within the fluid.

While polymers have been used in the past as gelling agents in fracturing fluids to carry or suspend solid particles in the brine, such polymers

require separate breaker compositions to be injected to reduce the viscosity. Further, such polymers tend to leave a coating on the proppant even after the gelled fluid is broken, which coating may interfere with the functioning of the proppant. Studies have also shown that "fish-eyes" and/or "microgels" present in some polymer gelled carrier fluids will plug pore throats, leading to impaired leakoff and causing formation damage.

Conventional polymers are also either cationic or anionic which present the disadvantage of likely damage to the producing formations.

It would be desirable if a composition and method could be devised to overcome some of the problems in the conventional injection of treatment fluids such as fracturing fluids.

Summary of the Invention

Accordingly, it is an object of the present invention to provide a non-polymer, non-ionic gelling agent for aqueous treatment fluids used in hydrocarbon recovery operations.

It is another object of the present invention to provide a gelling agent which may have improved viscosity breaking, higher sand transport capability, is more easily recovered after treatment, and has low potential for damaging the reservoir.

Still another object of the invention is to provide a gelling agent method which can be more easily mixed "on the fly" in field operations and does not require numerous co-additives in the fluid system.

In carrying out these and other objects of the invention, there is provided, in one form, a method for treating a subterranean formation which involves first providing an aqueous viscoelastic treating fluid having an aqueous base fluid and a non-ionic amine oxide surfactant gelling agent. The aqueous viscoelastic treating fluid is then injected through a wellbore and into the subterranean formation, and the subterranean formation is treated under conditions effective to do so.

Brief Description of the Drawings

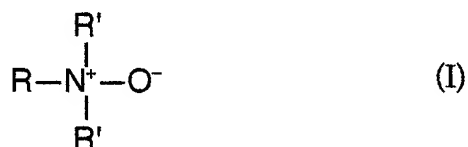
FIG. 1 is a graph of surfactant gel viscosity as a function of temperature; and

FIG. 2 is an additional graph of surfactant gel viscosity plotted as a function of temperature comparing an inventive amine oxide gelling agent with conventional gelling agents.

Detailed Description of the Invention

A new type of gelling agent has been discovered which will improve the fracturing (frac) fluid performance through the use of a polymer-free system. This system offers improved viscosity breaking, higher sand transport capability, is more easily recovered after treatment, and is relatively non-damaging to the reservoir. The system is also more easily mixed "on the fly" in field operations and does not require numerous co-additives in the fluid system, as do some prior systems. The new inventive system is non-ionic, while other fluids of this type are either cationic or anionic, which is an advantage over prior systems. Non-ionic fluids are inherently less damaging to the producing formations than cationic fluid types, and are more efficacious per pound than anionic gelling agents. The amine oxide technology of this invention has the potential to offer more gelling power per pound, making it less expensive than other fluids of this type.

The amine oxide gelling agents of the invention have the following structure (I):



Where R is an alkyl or alkylamido group averaging from about 8 to 24 carbon atoms and R' are independently alkyl groups averaging from about 1 to 6

carbon atoms. Preferably, R is an alkyl or alkylamido group averaging from about 8 to 16 carbon atoms and R' are independently alkyl groups averaging from about 2 to 3 carbon atoms. A particularly preferred amine oxide gelling agent is tallow amido propylamine oxide (TAPAO), which should be understood as a dipropylamine oxide since both R' groups are propyl.

The amine oxide gelling agents of the invention may be used in aqueous treatment fluids, particularly brines. The brine base fluid may be any brine, conventional or to be developed which serves as a suitable media for the various concentrate components. As a matter of convenience, the brine base fluid may be the brine available at the site used in the completion fluid, for a non-limiting example:

While the amine oxide gelling agents of the invention are described most specifically herein as having use in fracturing fluids, it is expected that they will find utility in acidizing fluids, gravel pack fluids, stimulation fluids and the like. Of course, when the treatment fluid is a fracturing fluids, the fluids also contain at least an effective amount of a proppant to prop open the fractures, and the fluid is injected into the formation under sufficient and effective hydraulic pressure and pump rate to fracture the formation. When the treatment fluid is an acidizing fluid, it further contains an effective amount of an acid, either inorganic or organic, of sufficient strength to acidize the formation. When the amine oxide gelling agents are used in a gravel packing fluid, the gelling agent helps contain an effective amount of the gravel within the fluid. If the amine oxide gelling agents are used in another well stimulation fluid, an effective amount of any additional stimulating agent is employed. When the amine oxide gelling agents are used in a fluid loss control application, an effective amount of a salt or easily removed solid is employed, and the amine oxide gelling agents help suspend the salts or solids in the fluid. These other components of the treatment fluids are well known in the art.

The effective proportion of the amine oxide gelling agents in the treatment fluids of this invention range from about 0.5 to about 25 vol. %, prefer-

ably from about 1 to about 10 vol. %, and most preferably about 6 vol. %. In a non-limiting example, a 6 vol.% solution of the gelling agent is mixed with brine, which is then blended with sand or other particulate, and pumped into a hydrocarbon bearing reservoir.

In one non-limiting embodiment of the invention, the non-ionic amine oxide gelling agents are the only gelling agents employed, although more than one may be used. In another non-limiting embodiment of the invention, the non-ionic amine oxide gelling agents are employed in the absence of polymeric gelling agents. In still another non-limiting embodiment of the invention, the non-ionic amine oxide gelling agents are employed in the absence of either cationic or anionic gelling agents.

In the method of this invention, breaking the gel of the aqueous viscoelastic treating fluid made using the amine oxides of this invention may be accomplished by a variety of mechanisms. These may include, but are not necessarily limited to, contacting the fluid with a hydrocarbon, contacting the fluid with alkoxylated alcohol solvents, dilution, such as with larger quantities of brine or water, or the addition of a reactive agent. The hydrocarbon may be the hydrocarbon produced from the formation or other hydrocarbon.

In another embodiment of the invention, the treatment fluid may contain viscosifying agents, other surfactants, clay stabilization additives, scale dissolvers, biopolymer degradation additives, and other common components.

The proppant, solid particle or gravel may be any solid particulate matter suitable for its intended purpose, for example as a screen or proppant, etc. Suitable materials include, but are not necessarily limited to sand, sintered bauxite, sized calcium carbonate, sized salts, ceramic beads, and the like, and combinations thereof. These solids may also be used in a fluid loss control application.

A basic method is to inject the proppant into a carrier fluid or treatment brine downstream from the conventional pumps which are delivering the gravel packing fluid, *e.g.* To do this, the proppant is suspended in the

viscosified brine. The proppant may thus be delivered by a small injection pump to the carrier fluid at an injection point downstream from the pumps used to transport the gravel packing fluid or other treatment fluid.

The invention will be further described with respect to the following Examples which are not meant to limit the invention, but rather to further illustrate it.

EXAMPLE 1

The following fluid was prepared in 3% KCl brine: 6 vol. % TAPAO. The surfactant gel viscosity of the fluids were measured on a Brookfield PVS viscometer at 100 sec⁻¹. The results are plotted on the chart of FIG. 1. It was surprisingly discovered that the viscosity of the fluids using the inventive gelling agents herein remains generally stable over the tested temperature range. It was also surprisingly discovered that the viscosity of the fluids using the inventive gelling agents herein remains generally stable over time as well. Five (5) hours was a typical test period for these tests.

EXAMPLES 2-8

The following fluids were prepared in 3% KCl brine:

Comparative Example 2: 3 vol. % Ethoquad E/12.

Example 3: 3 vol. % TAPAO of a 50 vol. % solution.

Example 4: 6 vol. % TAPAO of a 50 vol. % solution.

Comparative Example 5: 3 vol. % AROMOX DM16

Comparative Example 6: 6 vol. % AROMOX DM16

Comparative Example 7: 3 vol. % AROMOX C/12

Comparative Example 8: 6 vol. % AROMOX C/12

The AROMOX materials are polymeric quaternary ammonium halide salt gelling agents commercially available from Akzo-Nobel, Inc. AROMOX DM16 is a polymeric quaternary ammonium halide salt gelling agent have a C₁₆ substituent and two C₁ substituents on the nitrogen. AROMOX C/12 is a

polymeric quaternary ammonium halide salt gelling agent have a C₁₂ substituent and two C₁ substituents on the nitrogen.

The surfactant gel viscosity of the fluids were measured on a Fann 35 viscometer at 170 sec⁻¹. The results are plotted on the chart of FIG. 2. It can be seen again that the fluid of comparative Example 2 using Ethoquad E/12 loses viscosity as the temperature increases. It was again shown that the viscosity of the fluids using the inventive gelling agents herein remains generally stable over the tested temperature range. The viscosity of the fluids using the inventive gelling agents herein (Examples 3 and 4) was also higher and more stable than the comparative Examples 5-8 using commercially available AROMOX materials.

AROMOX E/12 and 50/50 mixtures of AROMOX C/12 with AROMOX E/12 at both 3 vol.% and 6 vol.% were also tested, but gave generally lower viscosities than AROMOX 16 at 3 vol.%.

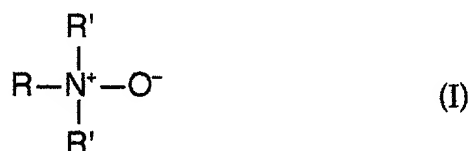
The inventive non-ionic, non-polymeric amine oxide gelling agents of this invention provide gelling stability over a wide temperature range and at relatively high temperatures. They are also expected to be relatively non-damaging to the formation since they are non-ionic.

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in providing a treatment fluid with stable surfactant gel viscosity. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific combinations of brines, amine oxides and other components falling within the claimed parameters, but not specifically identified or tried in a particular composition, are anticipated to be within the scope of this invention.

Claims

We Claim:

1. A method for treating a subterranean formation comprising:
 providing an aqueous viscoelastic treating fluid having:
 an aqueous base fluid; and
 a non-ionic amine oxide surfactant gelling agent;
 injecting the aqueous viscoelastic surfactant treating fluid through a
 wellbore and into the subterranean formation; and
 treating the subterranean formation under conditions effective to do
 so.
2. The method of claim 1 where the non-ionic amine oxide surfactant
 gelling agent is the only gelling agent employed.
3. The method of claim 1 where the non-ionic amine oxide surfactant
 gelling agent is employed in the absence of a polymeric gelling agent.
4. The method of claim 1 where the non-ionic amine oxide surfactant
 gelling agent is present in the aqueous base fluid in a proportion from about
 0.5 to about 25 vol. %.
5. The method of claim 1 where the non-ionic amine oxide surfactant
 gelling agent has the formula:



where R is an alkyl or alkylamido group averaging from about 8 to 24 carbon atoms and R' are independently alkyl groups averaging from about 1 to 6 carbon atoms.

6. The method of claim 1 where the non-ionic amine oxide surfactant gelling agent is tallow amido propylamine oxide (TAPAO).
7. The method of claim 1 where the aqueous base fluid is brine.
8. The method of claim 1 where treating the subterranean formation is selected from the group consisting of
 - fracturing the formation under effective pressure where the aqueous viscoelastic treating fluid further comprises a proppant;
 - acidizing the formation where the aqueous viscoelastic treating fluid further comprises an acid;
 - packing the formation with gravel where the aqueous viscoelastic treating fluid further comprises gravel;
 - stimulating the formation where the aqueous viscoelastic treating fluid further comprises a stimulating agent;
 - controlling fluid loss where the aqueous viscoelastic treating fluid further comprises a salt or easily removed solid; and mixtures thereof.
9. The method of claim 1 further comprising
 - breaking the gel of the aqueous viscoelastic treating fluid by a mechanism selected from the group consisting of contact with a hydrocarbon, contact with alkoxyated alcohol solvents, dilution, and contact with at least one reactive agent.

10. An aqueous viscoelastic treating fluid comprising:
an aqueous base fluid; and
a non-ionic amine oxide surfactant gelling agent.
11. The aqueous viscoelastic treating fluid of claim 10 in the absence of another gelling agent.
12. The aqueous viscoelastic treating fluid of claim 10 in the absence of a polymeric gelling agent.
13. The aqueous viscoelastic treating fluid of claim 10 where the non-ionic amine oxide surfactant gelling agent is present in the aqueous base fluid in a proportion from about 0.5 to about 25 vol. %.
14. The aqueous viscoelastic treating fluid of claim 10 where the aqueous base fluid is brine.
15. The aqueous viscoelastic treating fluid of claim 10 where the non-ionic amine oxide surfactant gelling agent has the formula:



where R is an alkyl or alkylamido group averaging from about 8 to 24 carbon atoms and R' are independently alkyl groups averaging from about 1 to 6 carbon atoms.

16. The aqueous viscoelastic treating fluid of claim 10 where the non-ionic amine oxide surfactant gelling agent is tallow amido propylamine oxide (TAPAO).

17. An aqueous viscoelastic treating fluid comprising:
 an aqueous base fluid; and
 a non-ionic amine oxide surfactant gelling agent having the formula:



where R is an alkyl or alkylamido group averaging from about 8 to 24 carbon atoms and R' are independently alkyl groups averaging from about 1 to 6 carbon atoms, and
 where the non-ionic amine oxide surfactant gelling agent is present in the aqueous base fluid in a proportion from about 0.5 to about 25 vol. %.

HYDRAULIC FRACTURING USING NON-IONIC SURFACTANT GELLING AGENT

Abstract of the Disclosure

It has been discovered that non-polymeric, non-ionic amine oxides, *per se*, are excellent gelling agents for treatment fluids for subterranean hydrocarbon formations. Treatment fluids with these gelling agents maintain their viscosity over increasing temperatures and time. A particularly preferred amine oxide is tallow amido propylamine oxide (TAPAO).

Fig. 1
Surfactant Gel Viscosity In 3% KCl Brine

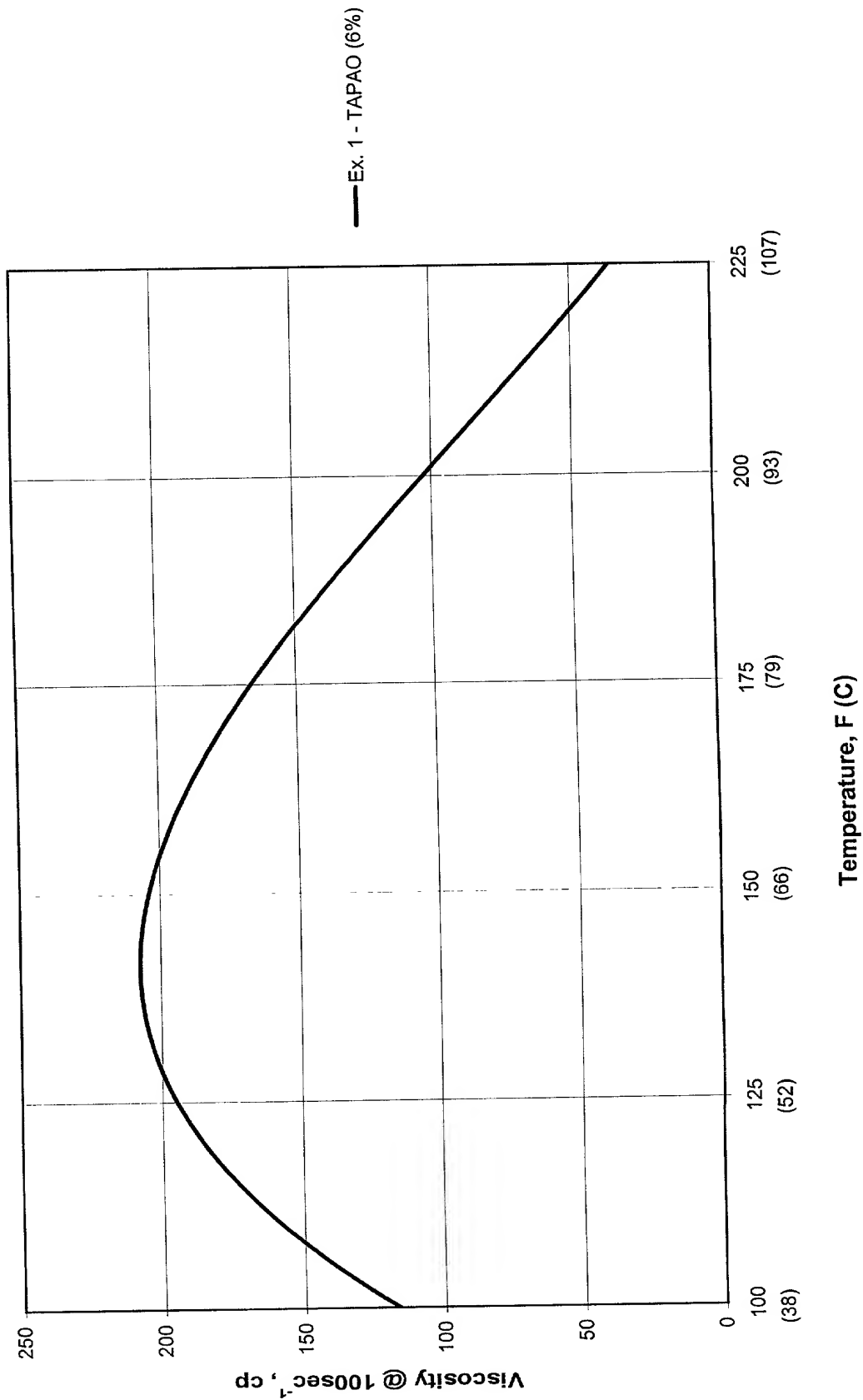
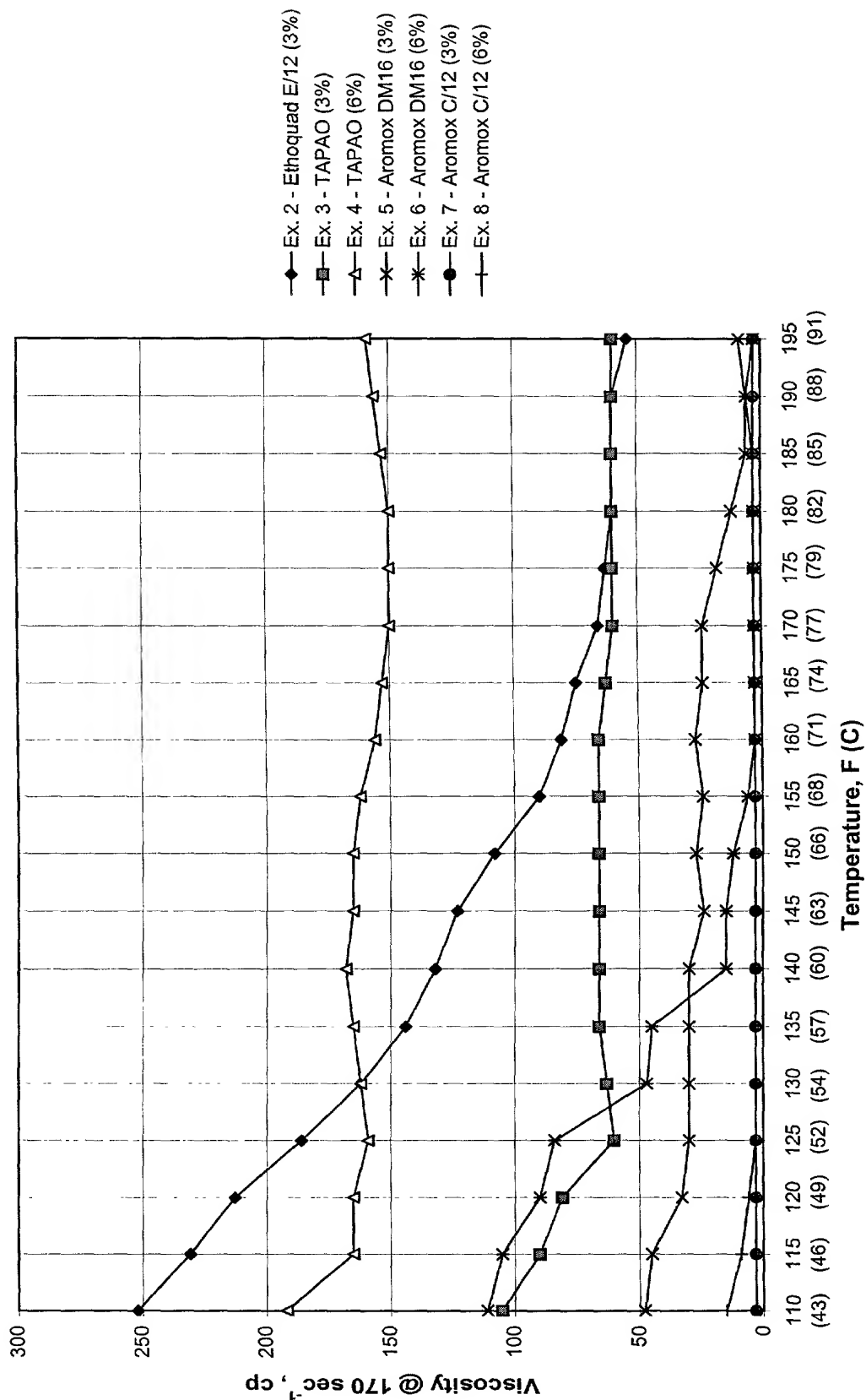


Fig. 2
Viscosities of 3% KCl brine on Fann 35 from 110 to 195F



DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As below named inventors, We hereby declare and say that:

Our residences, post office addresses and citizenships are as stated below next to our names,

We believe we are the original, first and joint inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**HYDRAULIC FRACTURING USING
NON-IONIC SURFACTANT GELLING AGENT
(304-15027-US),**

the specification of which

☒ [X] is attached hereto.

☐ [] was filed on _____ as Application Serial No. _____
as amended on _____.

☐ [] and amended by preliminary amendment attached hereto.

We hereby state that we have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

We acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

We hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed: NONE

Prior Foreign Application(s)

			Priority Claimed	
			[]	[]
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
_____	_____	_____	[]	[]
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

We hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the

filing date of the prior application and the national or PCT international filing date of this application: NONE

(Application Serial No.)	(Filing Date)	(Status) (Patented, pending, abandoned)

[] We hereby revoke all powers of attorney previously given.

We hereby appoint the following as our representatives to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith;

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 STEVEN G. MORGAN (Reg. No. 43,814); and
 G. MICHAEL ROEBUCK (Reg. No. 39,849).

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We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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